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A Comparison of Argo Merchant Oil and Sediment Hydrocarbons from Nantucket Shoals

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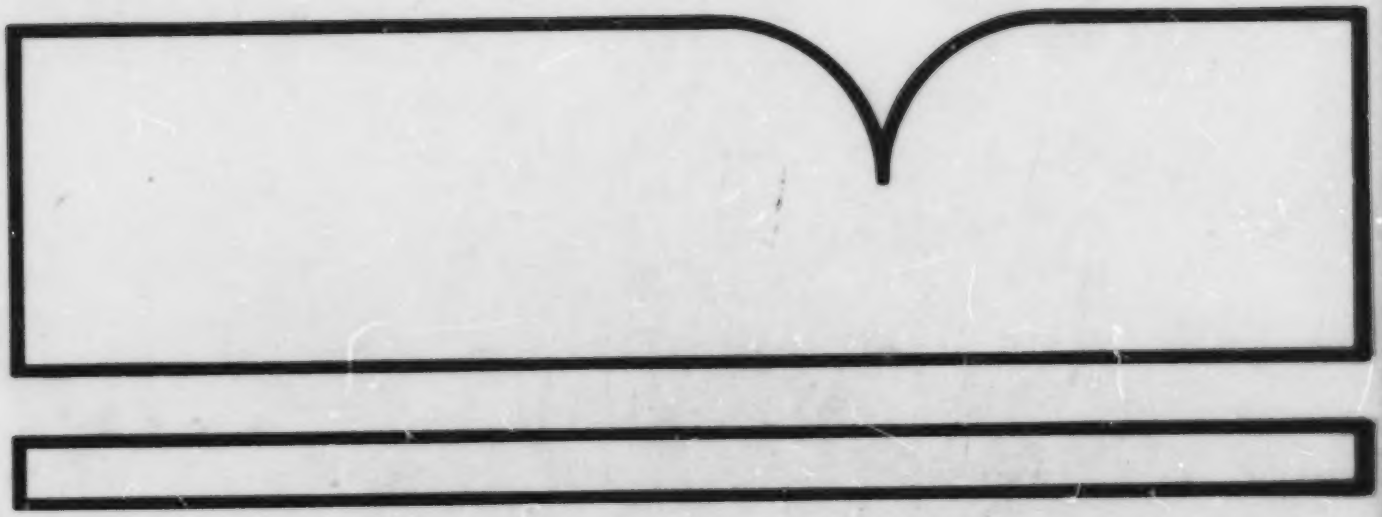

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16. ABSTRACT

Surface sediment samples collected from the Nantucket Shoals *Argo Merchant* wreck site area in February, 1977, were analyzed for hydrocarbon content by gas chromatography. Levels of hydrocarbons (n-C_{14} to n-C_{34} range) greater than 20 μg HC/gm dry weight sediment (ppm) were found at three stations, and traces of hydrocarbon contamination (0.7 to 1.1 ppm) were found at two other stations. Background levels in this area were less than 0.5 ppm. These findings indicate that significant hydrocarbon contamination extended at most 3-4 km from the wreck site in a SE direction. Traces of contamination were found 3-5 km from the wreck in the E and S directions. At the highly contaminated stations, the majority of hydrocarbons were in the form of minute tar particles mixed with sand. Analysis of sediment grab subsections revealed no clear trend of hydrocarbon contamination as a function of depth in sections as deep as 10 cm. Analyses of box core sections showed that contamination extended at least to 8-13 cm in depth. The stations which were found to contain significant hydrocarbon contamination in February were reoccupied on a cruise in July, 1977. Only the sediments at the bow section of the wreck site showed contamination (0.6 ppm) and these levels were significantly lower than found at this site in February (4 to 122 ppm).

The high degree of physical activity on the shoals is probably responsible for the areal patchiness and the inhomogeneous mixing of hydrocarbons with depth in the sediments. Although chemical, physical and biological weathering could be responsible for the observed decrease in hydrocarbon concentrations at the wreck site, turbulent mixing on the shoals probably transported the contaminated sediments out of the area or buried them under clean sand.

The chromatographically resolved hydrocarbon components of the tar particles and sediments were statistically compared with the resolved components of the *Argo Merchant* cargo oil. The hydrocarbons in the tar particles, and those sediments collected in February in the immediate vicinity of the wreck sites, matched well with the *Argo Merchant* cargo. The hydrocarbons in the sediments collected 3 km from the wreck in February and sediments collected at the wreck site in July match poorly with the cargo sample.

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Surface sediment samples collected from the Nantucket Shoals *Argo Merchant* wreck site area in February, 1977, were analyzed for hydrocarbon content by gas chromatography. Levels of hydrocarbons (n-C_{14} to n-C_{34} range) greater than 20 μg HC/gm dry weight sediment (ppm) were found at three stations, and traces of hydrocarbon contamination (0.7 to 1.1 ppm) were found at two other stations. Background levels in this area were less than 0.5 ppm. These findings indicate that significant hydrocarbon contamination extended at most 3-4 km from the wreck site in a SE direction. Traces of contamination were found 3-5 km from the wreck in the E and S directions. At the highly contaminated stations, the majority of hydrocarbons were in the form of minute tar particles mixed with sand. Analysis of sediment grab subsections revealed no clear trend of hydrocarbon contamination as a function of depth in sections as deep as 10 cm. Analyses of box core sections showed that contamination extended at least to 8-13 cm in depth. The stations which were found to contain significant hydrocarbon contamination in February were reoccupied on a cruise in July, 1977. Only the sediments at the bow section of the wreck site showed contamination (0.6ppm) and these levels were significantly lower than found at this site in February (4 to 122 ppm).

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Introduction

On December 15, 1976, the tanker *Argo Merchant* ran aground on Fishing Rip of Nantucket Shoals off the Massachusetts coast. Within one week she had broken into three parts, the stern and midsection remaining aground near the original point of impact and the bow section floating and eventually sinking 2.8 km SE of the stern section. During these events, approximately 28 x 10^3 metric tons of No. 6 fuel oil were spilled into the ocean. In order to determine the degree to which the sediments were contaminated in the vicinity of the wreck site and Little Georges Bank, the University of Rhode Island organized five cruises to the area. On several of the earlier cruises which collected sediments over a 4000 km^2 grid, the U.S. Coast Guard conducted on-board hydrocarbon screening using UV fluorescence spectroscopy, the results of which indicated that the sediments were contaminated with *Argo Merchant* oil only around the wreck site (Grose and Mattson, 1977). On the basis of these findings, a detailed sediment survey of the wreck site area was conducted on R/V *Endeavor* cruise 005, February 22-27, 1977. Several of these stations were reoccupied in July 22-24, 1977, five months later, on F/V *Sideshow* cruise 001.

The objectives of this study were as follows: (1) determination of the areal extent of surface sediment contamination by the *Argo Merchant* oil; (2) measurement of the depth of sediment contamination; and

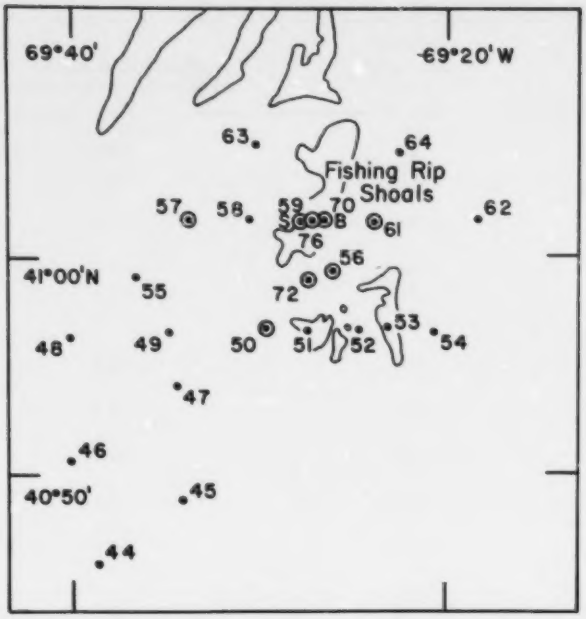

Figure 1. *Station locations of EN-005 (February 22-27, 1977), and SS-001 (July 2-24, 1977). The "S" (Station 59) is the location of the Argo Merchant stern and mid section wrecks and the "B" (Station 70) is the location of the Argo Merchant bow section. The circled dots are the stations from which the sediments analyzed in this study were collected. The other stations were analyzed by the U.S. Coast Guard.*

(3) evaluation of physical, chemical and/or biological weathering of the oil as a function of time.

Experimental Procedures

Sediment Sampling. Sediment samples were collected from the Nantucket Shoals *Argo Merchant* wreck site area aboard R/V *Endeavor* (EN-005, February 22-27, 1977) and aboard F/V *Sideshow* (SS-001, July 22-24, 1977) (Figure 1). Surface sediment samples (0-15 cm) were collected with a Smith-McIntyre grab sampler. One-half of each grab sample was preserved in formalin for biological archiving purposes. From the other half, used for chemical analysis, successive subsamples were placed into individual one quart Mason jars. The depths noted in the results section are estimates of the different depths in the grab sampler from which the individual subsamples were taken. After a small portion (5 cc) of each subsample was removed for on-board screening by Coast Guard personnel, the remainder of each subsample was frozen until later analysis (*Sideshow* sediment samples were stored in an ice locker while at sea and subsequently frozen upon return to the laboratory). Sediment cores (13-14 cm each) were obtained on EN-005 with a box corer. Three subsamples of each core were taken with plastic core liners. Two subsamples were used in benthic flux experiments. The third subsample, analyzed in this study, was frozen immediately after collection.

Cargo and Slick Sampling. One cargo sample and two surface slick samples were collected by Dr. Jerome Milgram of MIT who graciously provided subsamples of these for analysis and information on the collection and storage procedures (Milgram, personal communication, 1977). The *Argo Merchant* cargo oil sample was collected on December 19, 1976. The cargo sample, from the full port tank #4, was taken by putting a glass jar into the tank, withdrawing the jar and closing it. The first slick sample (Milgram #1) was collected on December 19, 1976, by lowering a bucket from the side of the USCGC *Vigilant*. The sample came from a distance of 2 to 4 km from the ship and Milgram estimates that it had been on the water for about one hour. The second sample (Milgram #2) was collected on December 25, 1976, at 40°54'N, 68°38.1'W, from a large pancake, also by lowering a bucket from the side of the USCGC *Vigilant*. It had probably been on the water for about four or five days. The cargo and slick samples were stored at room temperature in closed glass jars; after arrival in our lab, they were stored at 0°C until analyzed.

Sediment Analysis. Selected sediment samples from EN-005 were chosen for analysis on the basis of two criteria: (1) evidence of measurable or trace quantities of petroleum based on the Coast Guard screening results and/or (2) presence of minute tar particles which appeared on the top of the formalin surface of the biology subsample upon agitation of the sediment. Selection of SS-001 samples were based on (1) indications of contamination found on previous cruises and (2) stations adjacent to contaminated stations of earlier cruises. Occasionally minute tar particles (1 to 2 mm) were removed from the samples with tweezers prior to analysis, and the tar particles and sediment were analyzed separately.

After determination of the moisture content of a small portion of each sediment sample, 70-240 gms of wet sediment (50-200 gms dry weight) was weighed into a two ℓ round bottom flask. Generally 60 μg of *n*-C_{20} and 200 μg of *n*-C_{22} were added as internal standards for the EN-005 samples, and 20 μg of *n*-C_{20} and 100 μg of *n*-C_{22} were added as internal standards for the SS-001 samples. The samples were then saponified using 500-800 ml of a 70% 0.5 N KOH/methanol - 30% toluene mixture under reflux conditions for 2 hours. Enough water was added to the mixture (10 to 20% of the methanol) to prevent transesterification. The sediment-solvent mixture was allowed to cool and then filtered using a pre-ignited Whatman GF/C filter. The sediment and filter were washed with methanol, then with petroleum ether. The filtrate and combined washings were transferred to a two ℓ separatory funnel and separated into two phases by adding an amount of distilled water equal to the amount of methanol. The non-saponifiable fraction (petroleum ether-toluene phase) was separated from the saponifiable fraction (water-methanol phase) and the latter phase was extracted two additional times with petroleum ether. The petroleum ether extracts were combined and added to the non-saponifiable fraction and evaporated to dryness on a rotary evaporator at 35-40°C. The residue was charged to a column in one ml of a 95% petroleum ether-5% toluene mixture. This column, prepared in a Pasteur pipette, contained (from bottom to top) a glass wool plug, 0.3 gm Cu powder (activated with 3N HCl), 1 gm silica gel (deactivated with 5% water), 1 gm alumina

Table 1. Total hydrocarbons in selected sediment samples from Cruise EN-005. February 22-27, 1977.

Station (replicate)	*Latitude*	*Longitude*	*Depth of sediment (cm)*	*Total hydrocarbons µg/gm (dry wt sediment)*
50(1) G*	40° 57.1'N	69° 30.1'W	0-1	<0.1
50(2) G	40° 56.9'N	69° 29.9'W	0-1	0.8
50(2) G	"	"	1-3	0.4
50(2) G	"	"	3-5	<0.1
56(1) G	40° 59.2'N	69° 27.0'W	0-1	1.2
56(3) G	40° 59.2'N	69° 27.3'W	0-1	<0.3
56(4) G	40° 59.0'N	69° 29.0'W	0-1	21.5
57(1) G	41° 02.0'N	69° 33.5'W	0-1	<0.1
59(1) G	41° 02.5'N	69° 27.3'W	0-1	2.4†
59(1) G	"	"	1-3	0.5
59(1) G	"	"	3-5	<0.1†
59(3) G	41° 03.0'N	69° 27.5'W	0-1	2.6†
59(3) G	"	"	1-3	<0.1
59(3) G	"	"	3-5	<0.1
59(4) G	41° 02.9'N	69° 27.2'W	0-1	0.3
59(4) G	"	"	1-3	0.1
59(4) G	"	"	3-5	<0.1
59(1) BC**	41° 02.5'N	69° 27.0'W	0-3	5.1
59(1) BC	"	"	3-8	1.3
59(1) BC	"	"	8-13	24.6
59(2) BC	41° 02.6'N	69° 27.0'W	0-4	0.3
59(2) BC	"	"	4-9	0.8
59(2) BC	"	"	9-14	0.4
61(2) G	41° 02.6'N	69° 22.5'W	0-1	1.1
61(3) G	41° 01.0'N	69° 23.0'W	0-1	0.7
70(1) G	41° 01.8'N	69° 26.2'W	0-1	12.8
70(1) G	"	"	1-3	29.6
70(1) G	"	"	3-5	11.5
70(1) G	"	"	>5	19.7
70(3) G	41° 02.0'N	69° 26.6'W	0-1	10.2
70(3) G	"	"	1-3	4.0
70(3) G	"	"	3-5	5.6†
70(4) G	41° 02.0'N	69° 26.5'W	0-1	118, 69.7, 35.7††
70(4) G	"	"	1-3	5.1
70(4) G	"	"	3-5	122
70(1) BC	41° 02.0'N	69° 26.5'W	0-3	1.9
70(1) BC	"	"	3-8	2.7
70(1) BC	"	"	8-13	2.2
70(2) BC	41° 01.9'N	69° 26.3'W	0-3	2.7
70(2) BC	"	"	3-8	28.2
70(2) BC	"	"	8-13	37.5

**G = Smith-McIntyre grab samples*
† tarball removed prior to analysis
*** BC = box core samples*
†† triplicate analysis

(deactivated with 5% water), and another glass wool plug. The sample was eluted with 15 ml of the 95% petroleum ether-5% toluene mixture. It was found that this column procedure retained elemental sulfur, methyl esters, methyl ketones and more polar organic compounds while eluting hydrocarbons including *n*-alkanes, and aromatics, such as phenanthrene, pyrene and chrysene. The petroleum ether-toluene mixture was then evaporated to dryness and dissolved in methylene chloride. Each sample was analyzed by gas-liquid chromatography (GLC) with a Hewlett-Packard Model 5711A or 5840A gas chromatograph equipped with dual flame ionization detectors. Most of the analyses were accomplished using dual packed columns (2m, 2.2 mm i.d. stainless steel) containing 10% SP-1000 on Supelcoport, 80/100 mesh. A few analyses were done using a glass capillary column (15 m, 0.25 mm i.d., OV-101, Quadrex Corp.). The hydrocarbons measured eluted from the column between *n*-C_{14} and *n*-C_{34} using temperature programming from 90°C to 260°C at 8°/minute for the packed column and 60°C to 240°C at 4°/minute for the capillary column. The chromatograms were quantified by comparing the areas of the chromatograms with the areas of the *n*-C_{20} and/or *n*-C_{22} internal standards.

Procedural blanks were determined by carrying solvents and internal standards through the analysis procedure in the absence of the sediments. The average blank was 23 ± 10 μg/sample. Concentrations were reported for all sediment samples in which the blank correction represented <50% of the blank plus sample value. For a 200 gm sediment sample, this would yield a detection limit of approximately 0.1 ppm (23 μg/200 gm). Whenever the blank correction was greater than 50% of the total, the values were reported as less than the detection limit for that specific sediment sample weight. All the values reported in the tables have been corrected for the blank.

Cargo, Slick, and Tar Particle Analysis. After weighing, these samples were dissolved in the 95% petroleum ether-5% toluene mixture and charged to the Cu-silica gel-alumina column described previously. The hydrocarbon elutant was evaporated to dryness, dissolved in methylene chloride, and analyzed by GLC.

Results and Discussion

A. Areal Extent of Sediment Contamination. The locations where sediment was collected on EN-005 are given in Figure 1. Sediments from all of these stations were prescreened by Coast Guard personnel. This study presents detailed GLC analysis only on those samples found to have at least some trace of oil by the Coast Guard technique or those samples from which small tar particles floated out of the corresponding biological samples. A total of 45 subsamples from six EN-005 stations and 15 subsamples from six SS-001 stations were analyzed. These latter stations are also shown in Figure 1.

The present data (Table 1) indicate that in February, 1977, the sediments were significantly contaminated at 3 stations (56, 59, 70 - significantly defined as greater than 20 μg HC/gm dry weight, a value ranging from 40 to >200 times higher than the background hydrocarbon concentrations). Two of these stations were located at the wreck site locations: Station 59 at the original wreck site (now the location of the mid and stern sections); and Station 70, the location of the bow section. Station 56 is located 3.2 km SE of the bow section in the channel adjacent to Fishing Rip Shoal. The sediment at 59 and 70 was coarse sand while the sediment at 56 was gravel mixed with crushed shells and mud. Background hydrocarbon levels in the area were less than 0.5 μg/gm. Trace levels of petroleum (0.7 to 1.1 μg/gm) were found at Stations 50 and 61. (Station 50 was 4.8 km SW of the wreck; Station 61 was 3.2 km E of the wreck.) Both of these stations were located in the channel to the S and E of the wreck and the presence of traces of petroleum hydrocarbons at these locations could either be from sources other than the *Argo Merchant*, or from the *Argo Merchant* itself. Since the Coast Guard found no evidence of *Argo Merchant* oil at the other stations and, assuming that their results are correct, our findings would indicate that significant sediment contamination in February extended at most 3-4 km from the wreck site in a SE direction. Traces of contamination from an unknown source could be found 3-5 km from the bow in the E and SW directions. At most, this would indicate that in February, a 10-15 km^2 area of the sediments were contaminated. It is likely that only a small percentage of this area was significantly contaminated, these areas being limited primarily to the immediate vicinity of the wreck site, especially around the bow section.

B. Depth of Contamination. An attempt was made to determine the depth of sediment contamination by taking successive subsamples out of Smith-McIntyre grab samples or by examination of box cores. Neither sampling device collected sand any deeper than 13-20 cm, and in the case of gravel bottom stations, a maximum of only 3-4 cm of sediment was collected. No clear trend as a function of depth was noted in the EN-005 sediment samples. For example, at Stations 70(1)BC and 70(1)G, the hydrocarbon concentrations were fairly constant with depth, while at Stations 59(1)BC, 70(4)G, and 70(2)BC, the higher concentrations generally appear in the subsurface sediments, and at Stations 59(1)G and 59(3)G the highest concentrations appear in the surface sediments (Table 1). The probable reasons for this variation are: patchiness due to inhomogeneous mixing of minute tar particles into the sand, coupled with the highly active physical nature of the shoals. The tidal currents in this area at times exceed 3 knots. Such current speeds will result in erosion and transportation of coarse sand as found on the shoals and then deposition elsewhere as the current slackens (Heezen and Hollister, 1964). Then the tidal current reverses direction and the process occurs again, this time in an opposite direction. The depth to which this erosion-deposition cycle extends with each half tidal cycle has not been studied on Nantucket Shoals but has been shown to involve at least 2 meters on Middle Ground (a shoal in Vineyard Sound, Massachusetts), and at times sediments as deep as 6 meters can be moved (Smith, 1969). In this present study, it can only be concluded that contamination of some of the sediment extends at least to 8-13 cm in depth. Clearly, the possibility exists that the contamination could be significantly deeper than this.

C. Nature of Sediment Contamination. It was found that at least some of the petroleum hydrocarbons in the sediments were associated with minute tar particles. In order

Table 2. Comparison of total sediment hydrocarbon concentrations with and without inclusion of tar particles (EN-005 sediments).

Stat/Rep/Depth*	Total hydrocarbons µg/gm (dry wt sediment)		
	Sediment with tar particles physically removed	Tar contribution	Sediment with tar particle contributions included
59(1)0-1	2.4	73.5	75.9
59(1)3-5	<0.1	48.5	48.6
59(3)0-1	2.6	324	327
70(3)3-5	5.6	29.1	34.7

*all grab samples, depth in cm

to find out the approximate percentage of the total hydrocarbons these tar particles represented, particles were physically isolated with spatula and tweezers from four of the samples. The sediments (without their tar particles) and the tar particles were analyzed separately. The result of this experiment is given in Table 2. In all cases, the tar particle contribution to the sediments was the major contribution rather than any coating on the sand. It is also clear that the number and size of the tar particles in any one sediment sample is going to greatly affect the results. In order to minimize this problem, large sediment weights (usually 100 to ~ 200 gms) were used for each analysis in this study. In spite of this precaution, replicate analyses from the same subsample indicate variabilities of a factor of three. (See Station 70(4)0-1 in Table 1 for replicate analyses data.) Since the uncertainty for the analytical procedure is no greater than 10%, the sediment samples were inhomogeneous even when taken from the same storage container. This is undoubtedly one of the reasons, perhaps the major one, why the Coast Guard on-board screening analytical results do not agree in all cases with the results presented here. Although our values are generally lower, there is some correlation between the Coast Guard screening analysis and our analysis ($r = 0.69$ for 20 samples) in spite of the patchiness. The patchiness due to inhomogeneous mixing of the tar particles into the sand as a result of the physical activity of the area led to even greater variations from grab sample to grab sample even within 50 meters of each other. At Station 70, for example, the upper sediments (0-3 cm depth) in replicate grab and core samples contained 12.8, 10.2, 118, 1.9 and 2.7 µg/gm, a variation over two orders of magnitude. Thus the observed patchiness exists both on micro as well as a macro scale.

D. Comparison of Slick, Sediment and Tar Particle Samples with the Argo Merchant Cargo Oil. The chromatographically resolved portion of the hydrocarbon components of the tar particles, sediments and slick samples were compared with the resolved components of the *Argo Merchant* cargo oil, by a simple technique of comparing areas of each resolved component. It should be pointed out that the *Argo Merchant* carried two cargos, both No. 6 fuel oils, but only one of the cargos was sampled at the scene. It was this cargo sample that was used for matching purposes in this study. Although these oils were reported to be nearly identical (Grose and Mattson, 1977), some of the following matching experiments could have been affected by differences in the

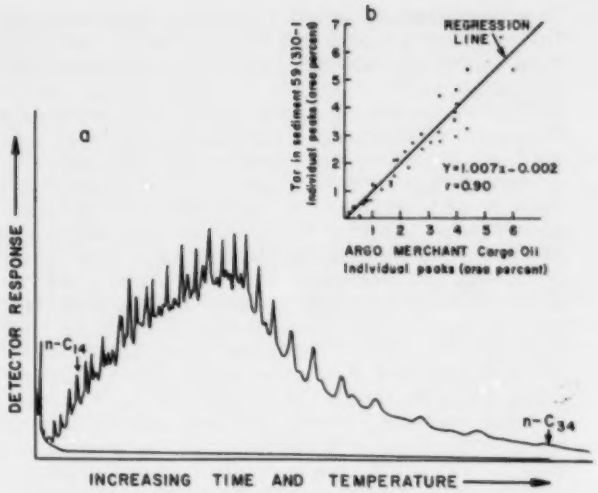

Figure 2. *Part A. Chromatogram (packed column) of tar particles separated from the sediment collected at Station 59, Grab 3, 0-1 cm depth, in February 1977. Part B. Graph of the areas of each resolved hydrocarbon component of this tar particle sample versus the area of the corresponding peaks in the Argo Merchant cargo.*

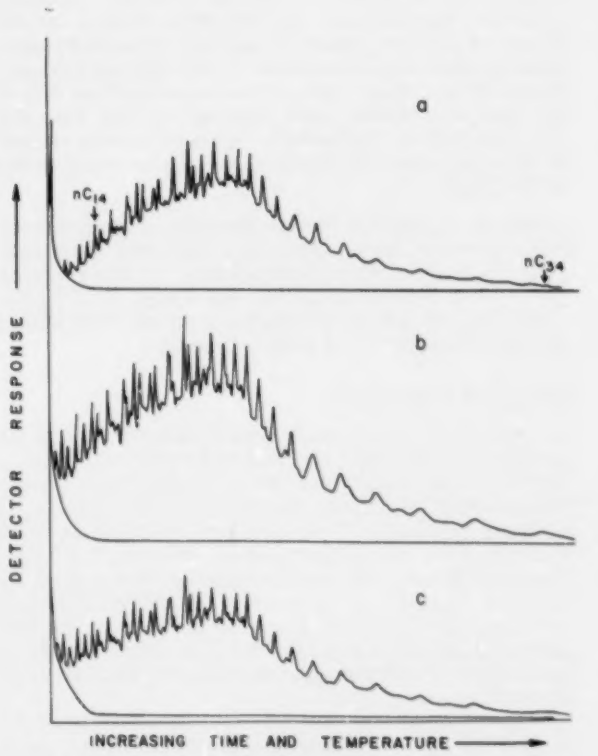

Figure 3. *Part A. Chromatogram (packed column) of the Argo Merchant cargo oil. Part B. Chromatogram (packed column) of a surface slick sample (Milgram #1) collected on December 19, 1976. Part C. Chromatogram (packed column) of a surface slick sample (Milgram #2) collected on December 25, 1976.*

Table 3. Comparison of resolved components in slick, sediment and tar particle samples with *Argo Merchant* cargo oil sample.

y	*y vs. Argo Merchant correlation coefficient*	*No. of area %'s*	*sig. level*
Argo Merchant duplicate analyses same day	0.99	31	>0.995
Argo Merchant duplicate analyses 2 days apart	0.97	38	>0.995
Argo Merchant duplicate analyses – same day	0.93*	17	>0.995
Oil sample on water one day (Milgram #1)	0.91	38	>0.995
Oil sample on water five days (Milgram #2)	0.96	39	>0.995
Tar – station 59 (1) 0-1 (EN-005)	0.89	24	>0.995
Tar – station 59 (1) 3-5 (EN-005)	0.79*	17	>0.995
Tar – station 59 (3) 0-1 (EN-005)	0.90	40	>0.995
Tar – station 70 (3) 3-5 (EN-005)	0.44	25	0.975
Sediment and tar station 70 (4) 3-5 (EN-005)	0.98	39	>0.995
Sediment without tar station 70 (3) 3-5 (EN-005)	0.74	27	>0.995
Sediment – station 59 (1) BC 8-13 (EN-005)	0.86	19	>0.995
Sediment – station 56 (4) 0-1 (EN-005)	0.21*	13	<0.95
Sediment – station 70 (1) 0-1 (SS-001)	0.18*	14	<0.95

**glass capillary major peaks*

resolved component pattern between the two cargos.

With the help of the HP-5840 integrator, the area of each peak (or resolved component) was expressed in area percent as per Equation (1):

$$A\%_i = \frac{A_i}{\Sigma A_i} \times 100\% \quad (1)$$

where $A\%_i$ is the area % of the individual resolved component, and A_i is the area in arbitrary units of each individual peak. The individual area percents of each peak of the standard (in this case, the *Argo Merchant* cargo oil sample collected by J. Milgram) are then plotted versus the corresponding area percents (using peaks having the same retention times) of the sample. All the reported peaks were used in the case of packed column chromatograms; however, only the major peaks (with area percentages greater than 1%) were included when glass capillary GLC was used. An example of the result is given in Figure 2. The area percents of each resolved peak in the chromatogram (Part A of Figure 2) were plotted versus the corresponding peaks in the cargo sample (Part A of Figure 3) to yield the resulting graph given in Part B, Figure 2. Visually the chromatograms look similar and linear least squares regression analysis of the individual area percents confirms a strong correlation ($r = 0.90$). An example of a poorer match is given in Figure 4. Here the resolved pattern of the sample visually does not look like the cargo sample. The peaks are less pronounced and in some places are absent altogether. Again the linear least squares regression analysis of the area percents of the resolved species indicates a poor correlation ($r = 0.44$). A summary of these examples and other samples compared to the *Argo Merchant* cargo is given in Table 3. Occasionally, a glass capillary column was used for the matching experiments. An example of the *Argo Merchant* oil chromatogram using glass capillary gas chromatography is given in Figure 5, part A.

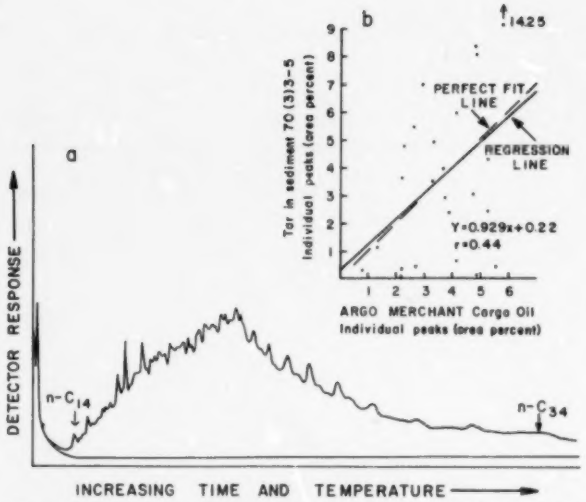

Figure 4. *Part A. Chromatogram (pecked column) of tar particles separated from the sediment collected at Station 70, Grab 3, 3-5 cm depth, in February, 1977. Part B. Graph of the areas of each resolved hydrocarbon component of this tar particle sample versus the area of the corresponding peaks in the Argo Merchant cargo.*

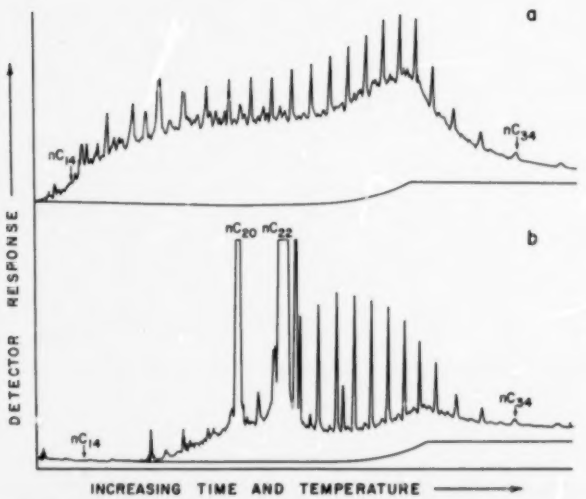

Figure 5. *Part A. Chromatogram (glass capillary column) of the Argo Merchant cargo oil. Part B. Chromatogram (glass capillary column) of the sediment collected at Station 70(1), 0-1 cm depth, in July, 1977. (The n-C_{20} and n-C_{22} are internal standards added for quantitation purposes.)*

In order to demonstrate the correlations obtained using duplicate injections, *Argo Merchant* cargo oil was analyzed using different injection conditions (as noted on Table 3). All of these procedures yielded strong correlations ($r > 0.90$) for *Argo Merchant* oil versus *Argo Merchant* oil. The chromatograms of the cargo and surface slick oil samples are given in Figure 3. Visually there is a strong resemblance and the correlations of the resolved area percents also confirms this strong correlation (Table 3). There is little evidence of weathering in slick samples up to 5 days. This is particularly interesting, since the *Argo Merchant* cargo contained about 20% of a cutter stock of light oil added to the No. 6 oil (Grose and Mattson, 1977). Apparently, there had not been substantial losses of these lighter components during the 5 days it was on the surface of the water. Undoubtedly the cold atmospheric temperature impeded the evaporative losses. (The mean temperature for these 5 days was -3°C, National Weather Service, Warwick, R.I.) In addition, the cold weather may have reduced the dissolution of the more potentially soluble components from the slick into the water column.

Three of the four tar particle samples also match well with the cargo oil ($r = 0.79$ to 0.90, Table 3). The other tar particle sample (sample 70 (3) 3-5, also shown in Figure 4), apparently had undergone some weathering, or was from a different source. The sediments collected around the wreck site matched well with the cargo although the sediment with the visible tar particles removed did not match as well as the other sediments from the wreck site. The hydrocarbons in the sediments collected 3 km from the wreck site in February (Station 56 (4)0-1, EN-005) did not match with the cargo oil; the chromatogram showed that either extensive weathering of the resolved peaks had taken place (if the hydrocarbons were *Argo Merchant* derived), or the hydrocarbons at this station were a weathered product of some other petroleum input. The hydrocarbons found in the sediments in July (Station 70 (1), SS-001) also did not match with *Argo Merchant* oil and the glass capillary chromatogram of these hydrocarbons is given in Figure 5, Part B. Visually there is little similarity between the resolved hydrocarbon pattern of the *Argo Merchant* cargo and this July sample. The July sediment pattern does, however, resemble patterns of tar lumps found on Bermuda beaches reported by Butler et al. (1973), patterns of tar particles >1 cm diameter in size in the N. Atlantic reported by Wade et al. (1976), and patterns for hydrocarbons in surface microlayers in coastal waters south of Martha's Vineyard in February, 1977 (Boehm, 1977). It can therefore only be concluded that the source of the hydrocarbons in the vicinity of the *Argo Merchant* wreck site in July is unknown. Clearly more information concerning the source of the hydrocarbons found in these environmental samples where poor matches were obtained could be learned if specific persistent compounds unique to the cargo could be found and studied in the samples.

E. Variation with Time. On July 22-24, 1977, five months after the R/V *Endeavor* cruise 005 in February, and seven months after the initial spill, further sediment samples from the wreck site areas were collected aboard F/V *Sideshow*. Samples were collected for chemical analysis and biological archiving at all the previously contaminated stations found on EN-005, with the exception of Stations 56 and 57 (where the July samples contained only cobbles and shell fragments). The hydrocarbon analytical results are given in Table 4. The samples all contained 0.6 μg HC/gm or less. Only at one station (Station 70 (1)) were traces of petroleum hydrocarbons found. An example of the chromatograms for this station is given in Figure 5B. Note that the chromatogram does not compare well with the *Argo Merchant* oil cargo chromatogram (Figure 5A), and there is no statistical correlation for the resolved components ($r = 0.18$,

Table 4. Total hydrocarbons in selected sediment samples from Cruise SS-001. July 22-24, 1977.

Station (replicate)*	*Latitude*	*Longitude*	*Depth of sediment (cm)*	*Total hydrocarbons µg/gm (dry wt sediment)*
50 (2)	40° 56.9'N	69° 30.1'W	0-1	0.1
59 (1)	41° 02.5'N	69° 27.8'W	0-1	0.2
59 (2)	"	"	0-1	<0.1
59 (3)	"	"	0-1	<0.2
61 (1)	41° 01.5'N	69° 24.3'W	0-1	0.4
70 (1)	41° 02.0'N	69° 26.8'W	0-1	0.5
70 (1)	"	"	1-3	0.6
70 (1)	"	"	3-5	0.6
70 (1)	"	"	5-10	0.4
70 (2)	41° 02.0'N	69° 26.8'W	0-1	0.2
70 (3)	41° 02.0'N	69° 26.8'W	0-1	<0.2
72 (2)	40° 59.2'W	69° 27.7'W	0-1	0.2
76 (1)	41° 02.0'N	69° 26.5'W	0-1	0.2
76 (2)	41° 02.4'N	69° 26.8'W	0-1	<0.2
76 (3)	41° 02.7'N	69° 27.7'W	0-1	0.4

**all grab samples*

Table 3). Since this sediment sample was collected at the *Argo Merchant* bow section wreck site station, it is tempting but highly unlikely to conclude that this is *Argo Merchant* oil after 7 months of physical and chemical weathering and/or biological degradation. This is unlikely since the *n*-alkanes which appear predominantly in the sample are usually the first to degrade with time relative to the complex mixture of cycloparaffins, aromatics and naphtheno-aromatics. These hydrocarbons could have been from non-cargo sources of oil from the *Argo Merchant* (i.e. hydraulic fluids, etc.) or from non-*Argo Merchant* sources altogether. With the exception of this station (Station 70(1)), the rest of the samples gave no evidence of petroleum hydrocarbons, weathered or otherwise, above the normal background levels.

Since the fishing vessel had a draft of only 2 meters, it was possible to collect sediment samples on top of the shoal, between the bow and stern section locations, a feat not possible with R/V *Endeavor* (draft of over 5 meters). Stations 76(1), 76(2), and 76(3) represent a transect across the shoal from the bow site to the stern site. It was felt that sediments at these stations might have been heavily contaminated with oil as the bow section drifted over them before it was sunk (Grose and Mattson, 1977). In July, no evidence of such contamination was found. Again because of the turbulence of the area, the oil could have been degraded, buried or transported away from the shoal, especially since seven months had passed from the time of the original spill.

No evidence of either transportation to other adjacent stations (50, 61, 72) or burial at the wreck site was found. Again, since we obtained sediments only as deep as 10 cm, it is unwarranted to make conclusions based on such samples when daily fluctuations in sediments of two meters are possible.

In summary, the hydrocarbon concentrations in the surface sediments in the vicinity of the *Argo Merchant* wreck site in July, 1977, were significantly lower than found on the earlier cruise in February. At only one station was evidence of petroleum hydrocarbon contamination found, and these hydrocarbons did not match the *Argo Merchant* cargo oil.

F. Mass Balance Considerations. A rough estimate of the percentage of spilled oil which became incorporated in the sediments can be made if a series of assumptions are used. Generally these assumptions tend to maximize the amount of oil in the sediments: (1) Assume an average concentration of hydrocarbons in the vicinity of the wreck (Stations 59 and 70) in February, 1977, is 16 ppm (arithmetic mean ± the standard deviation was 16 ± 30 ppm); (2) Assume a linear rate of weathering or dispersal with time, such that 16 ppm in February decreased to an average of 0.3 ppm in July in a linear decrease (extrapolation of this date back to December, 1976, produces an average minimum value hydrocarbon concentration of 22 ppm); (3) Assume an affected area of 15 km^2; (4) Assume a depth of contamination of 15 cm, and a constant concentration of hydrocarbons with depth; and (5) The average sediment density is approximately 3 gm/cm^3. Using these assumptions, it was calculated that a maximum of 1.5×10^2 metric tons of oil was incorporated in the sediments, or 0.5% of the total oil spilled. It is felt that this amount represents a maximum estimate .This calculation would therefore indicate that surface sediments in the vicinity of the wreck site were not a major sink for the oil in the case of the *Argo Merchant* oil spill.

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